

Grandreefite, pseudograndreefite, laurelite, and aravaipaite: Four new minerals from the Grand Reef mine, Graham County, Arizona

ANTHONY R. KAMPF

Mineralogy Section, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, U.S.A.

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

EUGENE E. FOORD

U.S. Geological Survey, Mail Stop 905, Denver Federal Center, Lakewood, Colorado 80225, U.S.A.

ABSTRACT

Four new lead fluoride minerals are described from the Grand Reef mine, Laurel Canyon, Aravaipa mining district, Graham County, Arizona. They occur together in a vug surrounded by layers of quartz, fluorite, and galena. The new minerals are interpreted as resulting from the reaction of supergene solutions with galena and fluorite.

Grandreefite, $\text{Pb}_2\text{SO}_4\text{F}_2$, is orthorhombic, $a = 4.439(4)$, $b = 13.575(13)$, $c = 4.333(4)$ Å, $V = 261.1(4)$ Å³, space group $I222$, $Z = 2$. It occurs as colorless prismatic crystals striated parallel to $[001]$, with a density of $7.0(1)$ g/cm³ (meas.), 7.15 g/cm³ (calc.). Grandreefite is biaxial (+), very small $2V$, with weak dispersion, $r > v$, $\alpha = 1.872(5)$, $\beta = 1.873(5)$, $\gamma = 1.897(5)$; orientation is $X = c$, $Y = a$, $Z = b$. The composition is PbO 82.9, SO₃ 13.8, F 7.1, sum 103.8, less O = F 3.0, total 100.8 wt%. Grandreefite is isostructural with $\text{La}_2\text{O}_2\text{SO}_4$, based on layers of the β -PbF₂ (fluorite) structure parallel to (010) with SO₄ groups between layers.

Pseudograndreefite, $\text{Pb}_6\text{SO}_4\text{F}_{10}$, is orthorhombic, $a = 8.5182(5)$, $b = 19.5736(11)$, $c = 8.4926(5)$ Å, $V = 1416.0(1)$ Å³, space group $F222$, $Z = 4$. It occurs as colorless square crystals tabular on $\{010\}$, with a density of $7.0(1)$ g/cm³ (meas.), 7.08 g/cm³ (calc.). Pseudograndreefite is biaxial (+), $2V = 30(3)^\circ$, with strong dispersion, $r > v$, $\alpha = 1.864(5)$, $\beta = 1.865(5)$, $\gamma = 1.873(5)$; orientation is $X = c$, $Y = a$, $Z = b$. The composition is PbO 84.9, SO₃ 4.7, F 13.1, sum 102.7, less O = F 5.5, total 97.2 wt%. The structure of pseudograndreefite is very similar to that of grandreefite.

Laurelite, $\text{Pb}(\text{F},\text{Cl},\text{OH})_2$, is hexagonal, $a = 10.252(9)$, $c = 3.973(1)$ Å, $V = 361.7(6)$ Å³, space group $P6$, $P\bar{6}$, or $P6/m$, $Z = 6$. It occurs as colorless needles with a density of $6.2(1)$ g/cm³ (meas.), 6.52 g/cm³ (calc.). Laurelite is uniaxial (+), with $\omega = 1.903(5)$, $\epsilon = 1.946(5)$. The composition is Pb 82.0, F 13.0, Cl 3.6, OH 0.9, total 99.5 wt%. The structure of laurelite is probably related to that of α -PbF₂.

Aravaipaite, $\text{Pb}_3\text{AlF}_9 \cdot \text{H}_2\text{O}$, is triclinic, with $a = 5.842(2)$, $b = 25.20(5)$, $c = 5.652(2)$ Å, $\alpha = 93.84(4)$, $\beta = 90.14(4)$, $\gamma = 85.28(4)^\circ$, $V = 827(2)$ Å³, space group $P1$ or $P\bar{1}$, $Z = 4$. It occurs as colorless thin plates with perfect micaceous $\{010\}$ cleavage and a density of 6.37 g/cm³ (calc.). Aravaipaite is biaxial (-), $2V = 70(3)^\circ$, with strong dispersion, $r < v$, $\alpha = 1.678(2)$, $\beta = 1.690(2)$, $\gamma = 1.694(2)$; Euler angles are $\phi = 67^\circ$, $\psi = 60^\circ$, $\theta = 76^\circ$. The composition is Pb 73.8, Al 3.6, F 21.0, H₂O 3.0, total 101.4 wt%. The structure of aravaipaite may be related to that of β -PbF₂ with layers of the β -PbF₂ structure parallel to $\{010\}$ and Al(F,H₂O) octahedra between layers.

INTRODUCTION

The Grand Reef mine is situated in Laurel Canyon, about 6 km northeast of Klondyke, in the Aravaipa mining district of Graham County, Arizona. The mine exploits a small epithermal lead-copper-silver deposit, which is hosted by a silicified breccia. The breccia is highly resistant, forming a precipitous cliff, locally known as the "reef," from which the name of the mine is derived. Dur-

ing the past 25 years, the mine has become well known among mineral collectors for a variety of rare minerals. The most notable of these is linarite, which has been found in well-formed crystals up to 5 cm in length. Jones (1980) provided an overview of the history, geology, and mineralogy of this deposit.

During the course of a detailed mineralogic and paragenetic study of the Grand Reef mine, Mr. William Besse (Besse, 1981) obtained an unusual specimen, which had

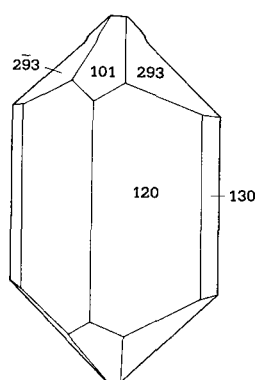


Fig. 1. Crystal drawing of grandreefite.

been recovered in 1980 by Mr. Wayne Thompson under the auspices of Southwestern Mineral Associates. Mr. Besse brought the specimen to the attention of one of us (A.R.K.) with the observation that it might contain two minerals new to science. In the course of the present investigation, these two minerals, as well as two others on the same specimen, were determined to be new. The four new minerals are named grandreefite, pseudograndreefite, laurelite, and aravaipaite. Grandreefite is named for the Grand Reef mine. Pseudograndreefite is named for its close similarity to grandreefite in physical properties, composition, and structure. Laurelite is named for Laurel Canyon in which the Grand Reef mine is situated. Aravaipaite (är á ví' pá ít) is named for the Aravaipa mining district in which the mine is located.

The species and the names were approved by the Commission on New Minerals and Mineral Names, IMA, prior to publication. The type specimen containing all four species is deposited at the Natural History Museum of Los Angeles County (cat. no. 25414).

GEOLOGIC AND MINERALOGIC SETTING

The ore at the Grand Reef mine was emplaced in a heavily brecciated, nearly vertical fault zone. The breccia, consisting of rhyolite and schist fragments, has been silicified and contains specular hematite and fluorite as the principal gangue minerals. The most prevalent primary ore mineral is galena, with chalcopyrite, argentite, and pyrite being present in lesser amounts. Chalcocite, covellite, silver, and copper were products of supergene enrichment. In addition to the four new minerals described here, Besse (1981) listed 25 other minerals, most of which have resulted from oxidation.

In 1969 a bench was blasted near the top of the "reef" just south of a vertical stope known as the "glory hole." The area of this bench has produced most of the mine's well-crystallized oxidation minerals, predominantly sulfates. The type specimen of the four new minerals was found in this area.

The type specimen measures $10 \times 7 \times 4$ cm, and the vug containing the new minerals is about $2 \times 1.5 \times 0.5$ cm. A second specimen with a $5 \times 2 \times 1.5$ cm vug was

subsequently provided for examination by its current owner, Mr. Les Presmyk of Mesa, Arizona. The two specimens were discovered to be portions of the same vug. To date these are the only specimens known to contain any of these new minerals. Fragments of rock trimmed from the second specimen were also provided. A block of matrix measuring $27 \times 25 \times 15$ cm was reconstructed from these fragments and the two vug sections.

The matrix is typical of the mineralization found in the bench area of the Grand Reef mine. Veins of galena follow irregular fractures in the breccia, and minor amounts of copper sulfides associated with the galena are altered principally to linarite and caledonite. The galena shows lesser alteration to anglesite. The vug containing the new minerals occupies the center of what was evidently once an interstice between breccia blocks. Although a portion of the rock surrounding the vug is missing, it is clear that the vug was completely surrounded by galena. An irregular and incomplete layer of fluorite is found inside the galena, followed by a complete layer of quartz surrounding the quartz-lined vug. Anglesite fills fractures in the quartz. A completely filled pocket surrounded by galena and containing only massive fluorite occurs a few centimeters away from the vug.

Isolated pockets in galena, sometimes containing vugs, are typical of the bench area of the Grand Reef mine, and the mineralization in these pockets is often quite distinct from that in the adjacent portions of the oxidation zone. Mr. Wayne Thompson (personal communication, 1988) has considered the vug containing the four new minerals to be an example of such an occurrence.

GRANDREEFITE ($\text{Pb}_2\text{SO}_4\text{F}_2$)

Appearance and physical properties

The only crystal of grandreefite on the type specimen measures $1.5 \times 3 \times 4$ mm parallel to the [100], [010], and [001] cell directions, respectively. The characterization of the mineral used fragments removed from this crystal, which is prismatic and striated parallel to [001]. The forms {120}, {130}, {293}, {293}, and {101} were observed and are depicted in Figure 1. Two bladelike crystals of grandreefite on the second specimen reach 7 mm in length.

Grandreefite is colorless and has a white streak. It is transparent with a subadamantine luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is approximately $2\frac{1}{2}$. The mineral is brittle with a conchoidal fracture, and no cleavage was detected. The density, measured on a Berman balance using 3.43 mg of sample, is $7.0(1)$ g/cm³; the calculated density is 7.15 g/cm³.

Optical properties

The optical properties of grandreefite were determined by immersion using a Supper spindle stage. Over the course of a few minutes, the crystal surfaces became frosted because of reaction with the high-index immersion liquids. This required that observations be made rapidly and may have contributed to experimental error.

TABLE 1. X-ray powder-diffraction data for grandreefite

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>
10	6.73	6.78	020	10	1.581	1.581	260
30	4.20	4.21	110	25	1.545	1.545	202
25	4.10	4.11	011	<5	1.508	1.506	222
10	3.382	3.389	040	5	1.468	1.467	310
100	3.159	3.162	130	20	1.424	1.426	190
90	3.116	3.120	031			1.422	091
80	3.084	3.090	101	30b	1.401	1.403	330
<5	2.810	2.811	121	10	1.377	1.396	301
50	2.281	2.283	141			1.381	271
5	2.254	2.259	060	10	1.370	1.370	033
30	2.209	2.213	200	50b	1.370	1.370	172
30	2.158	2.157	002			1.368	103
5	2.101	2.104	220	10	1.291	1.291	341
5	2.058	2.056	022			1.275	262
15	1.949	1.949	211	25b	1.274	1.268	143
10	1.922	1.920	112	5	1.242	1.241	1·10·1
5	1.854	1.853	240	<5	1.215	1.213	312
50	1.824	1.824	161	<5	1.194	1.196	291
60	1.806	1.805	231	20	1.188	1.190	192
		1.782	132			1.188	361
35b	1.780	1.774	170	15	1.176	1.176	332
		1.767	071	10	1.168	1.170	163
						1.165	233

Note: 114.6-mm Gandolfi camera, CuK α radiation, visually estimated intensities, indexed with the aid of the structure-factor data; b = broad line.

Grandreefite is optically biaxial (+). The indices of refraction measured in white light are $\alpha = 1.872(5)$, $\beta = 1.873(5)$, and $\gamma = 1.897(5)$. The observed $2V$ was very small; the calculated $2V$ is 23° . Weak dispersion, $r < v$, was observed. The optical orientation is $X = c$, $Y = a$, $Z = b$. Coarse polysynthetic twinning was observed under crossed polarizers, but no twin law could be determined and no morphological or X-ray diffraction evidence for twinning was found.

Chemical data

Grandreefite was analyzed with an electron microprobe utilizing synthetic PbO, celestite, and synthetic CaF₂ as standards for Pb, S, and F, respectively. The analysis yielded PbO 82.9, SO₃ 13.8, F 7.1, sum 103.8, less O \equiv F 3.0, total 100.8 wt%. Single-crystal infrared spectroscopy indicated that no water was present in the mineral (<0.001 wt%). The empirical formula based upon O + F = 6 is Pb_{2.07}S_{0.96}O_{3.92}F_{2.08}. The simplified formula, Pb₂SO₄F₂, requires PbO 81.39, SO₃ 14.60, F 6.93, sum 102.92, less O \equiv F 2.92, total 100.00 wt%. Grandreefite decomposes in cold water.

Crystallography

Precession photographs showed grandreefite to be orthorhombic, with the space group $I222$, $I2_12_12_1$, $Im\bar{m}2$, or $Im\bar{m}m$. The structure determination showed the space group to be $I222$. The cell parameters were refined using four-circle diffractometer data, yielding $a = 4.439(4)$, $b = 13.575(13)$, and $c = 4.333(4)$ Å. The cell volume is 261.1(4) Å³ and $Z = 2$.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuK α ra-

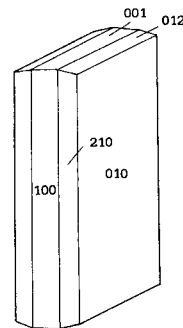


Fig. 2. Crystal drawing of pseudograndreefite.

diation was employed, and the intensities were visually estimated. These data along with the calculated d values are given in Table 1.

Comments on the structure

Grandreefite is apparently isostructural with La₂O₂SO₄ and may briefly be described as consisting of layers of the β -PbF₂ (fluorite) structure parallel to (010), with SO₄ groups between layers. The layer sequence corresponding to one unit cell is [SO₄-Pb-2F-Pb-SO₄-Pb-2F-Pb]. The La₂O₂SO₄ structure was determined by Fahey (1976) using powder-diffraction data, but the positional parameters that he assigned to the sulfate oxygen site must be considered suspect because of the large temperature factor (15) for this atom. An attempt to solve the structure of grandreefite using single-crystal data failed to locate the oxygen site(s) and has resulted in an R value of 0.11. It is likely that absorption-correction problems are largely to blame, but it is possible that either rotational disorder or twinning has obscured the site. Efforts are still under way to completely solve the structure.

PSEUDOGRANDREEFITE (Pb₆SO₄F₁₀)

Appearance and physical properties

Pseudograndreefite occurs as square (pseudotetragonal) crystals tabular on {010}. The tablets form a single subparallel aggregate on the type specimen measuring 4 × 1 × 4 mm parallel to the [100], [010], and [001] cell directions, respectively. The pseudograndreefite aggregate is in contact with the grandreefite crystal and appears to have partially overgrown the grandreefite. The forms {010}, {100}, {001}, {210}, and {012} were observed on pseudograndreefite crystals, as depicted in Figure 2. No twinning was detected.

The physical properties of pseudograndreefite are nearly identical to those of grandreefite. It is transparent and colorless with a subadamantine luster and a white streak. It exhibits no fluorescence in ultraviolet light and has a Mohs hardness of approximately 2½. It is brittle with a conchoidal fracture and no discernible cleavage. The density, measured on a Berman balance using 4.41 mg of sample, is 7.0(1) g/cm³; the calculated density is 7.08 g/cm³.

TABLE 2. X-ray powder-diffraction data for pseudograndreefite

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>
10	9.75	9.82	020			1.782	0·10·2
<5	4.90	4.91	040	70b	1.779	1.781	2·10·0
<5	4.23	4.25	002			1.771	244
		4.23	200			1.767	442
20	3.89	3.90	022	5	1.694	1.694	193
		3.89	220			1.691	391
<5	3.262	3.272	060	10	1.606	1.607	084
		3.213	042			1.602	480
100	3.204	3.205	240	5	1.527	1.527	0·12·2
30	2.999	2.999	202			1.526	2·12·0
5	2.447	2.454	080	5	1.503	1.499	404
25	2.212	2.211	262	<5	1.465	1.465	1·13·1
20	2.123	2.125	004	<5	1.404	1.402	0·14·0
		2.116	400			1.365	2·10·4
5	2.051	2.050	191			1.363	4·10·2
20	1.900	1.899	282	25b	1.364	1.363	464
5	1.865	1.865	224			1.361	046
		1.860	422			1.357	640
				5	1.346	1.344	206
						1.339	602

Note: 114.6-mm Gandolfi camera, CuK α radiation, visually estimated intensities, indexed with the aid of the structure-factor data; b = broad line.

Optical properties

The optical properties of pseudograndreefite were determined by immersion using a Supper spindle stage. Pseudograndreefite exhibited the same surface deterioration in high-index immersion liquids noted for grandreefite.

Pseudograndreefite is optically biaxial (+). The indices of refraction measured in white light are $\alpha = 1.864(5)$, $\beta = 1.865(5)$, and $\gamma = 1.873(5)$. The observed $2V$ is $30(3)^\circ$; the calculated $2V$ is 39° . Strong dispersion, $r > v$, was observed. The optical orientation is $X = c$, $Y = a$, $Z = b$. The lower indices of refraction, larger $2V$, and stronger dispersion are useful in distinguishing pseudograndreefite from grandreefite.

Chemical data

Pseudograndreefite was analyzed with an electron microprobe utilizing the same standards as for grandreefite. The analysis yielded PbO 84.9, SO₃ 4.7, F 13.1, sum 102.7, less O \equiv F 5.5, total 97.2 wt%. Single-crystal infrared spectroscopy indicated that no water was present (<0.01 wt%). The empirical formula based upon O + F = 14 is Pb_{5.91}S_{0.91}O_{3.29}F_{10.71}. The simplified formula, Pb₆SO₄F₁₀, requires PbO 87.57, SO₃ 5.24, F 12.42, sum 105.23, less O \equiv F 5.23, total 100.00 wt%. Pseudograndreefite decomposes in cold water.

Crystallography

Precession photographs showed pseudograndreefite to be orthorhombic with the space group $F222$, $Fmm2$, or $Fmmm$. The structure determination showed the space group to be $F222$. The cell parameters were refined using four-circle diffractometer data yielding $a = 8.5182(5)$, $b = 19.5736(11)$, and $c = 8.4926(5)$ Å. The cell volume is $1416.0(1)$ Å³ and $Z = 4$.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter and CuK α radiation. The intensities were visually estimated. These data and the calculated d values are given in Table 2.

Comments on the structure

As for grandreefite, the pseudograndreefite structure has as yet resisted complete solution. All Pb and S atoms have been located, as have most F atoms; but the oxygen atoms in the presumed sulfate group and the "interlayer" F atoms have not been located. The resulting R value is 0.11. The structure of pseudograndreefite is very similar to that of grandreefite and may briefly be described as consisting of layers of the β -PbF₂ (fluorite) structure parallel to (010) with SO₄ and F between layers. The layer sequence corresponding to one unit cell is [(2SO₄,4F)-4Pb-8F-4Pb-8F-4Pb-(2SO₄,4F)-4Pb-8F-4Pb-8F-4Pb]. Efforts are still under way to completely solve the structure.

LAURELITE (Pb(F,Cl,OH)₂)

Appearance and physical properties

Laurelite occurs as needles up to 10 mm long and 0.05 mm in diameter, but most needles are much thinner and are typically grouped in parallel bundles. Laurelite needles in loose jackstraw-fashion fill the interior of the vug surrounding and atop the crystals of grandreefite and pseudograndreefite. Laurelite needles are also found included in plates of aravaipate and, to a lesser extent, in crystals of pseudograndreefite.

The needles are prismatic parallel to [001] and have basal {001} terminations. Because of a combination of twinning, parallel growth, and narrowness, no distinct goniometer signals could be obtained from the prism faces. The crystals are twinned by rotation around [001].

Laurelite is colorless and has a white streak. It is transparent with a silky luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is approximately 2. The tenacity can best be described as brittle, although the needles are slightly flexible. The fracture is conchoidal and an imperfect {001} cleavage was observed. A pycnometer was used for the density determination. The measurement on a 9-mg sample yielded $6.2(1)$ g/cm³. The calculated density is 6.52 g/cm³. The discrepancy may be attributable to the difficulty in handling the needles and to small sample size.

Optical properties

The optical properties of laurelite were determined by immersion. No crystals suitable for conoscopic observation were found, but the mineral is assumed to be uniaxial because of its hexagonal symmetry. The optic sign is positive, and the indices of refraction measured in white light are $\omega = 1.903(5)$ and $\epsilon = 1.946(5)$. Laurelite was stable in high-index immersion liquids during the course of optical study.

TABLE 3. X-ray powder-diffraction data for laurelite

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>
<5	5.07	5.13	110	<5	1.651	1.650	302
<5	4.40	4.44	200	5*	1.595	1.595	510
<5	4.01	3.97	001	5*	1.570	1.570	222
25	3.61	3.63	101	5*	1.570	1.570	331
100	3.33	3.36	210	<5	1.542	1.546	312
40	3.125	3.140	111	<5	1.542	1.546	421
40	2.949	2.961	201	10*	1.481	1.480	402
		2.960	300	10*	1.422	1.422	520
30	2.559	2.564	211	35*	1.388	1.387	601
		2.563	220	5*	1.371	1.370	431
<5	2.457	2.463	310	15*	1.339	1.339	521
10	2.369	2.374	301			1.282	113
5	2.213	2.220	400			1.282	422
<5	2.147	2.154	221	40	1.282	1.282	611
35	2.090	2.093	311			1.282	440
5	2.034	2.037	320	15*	1.268	1.269	203
15	1.986	1.987	002			1.268	700
		1.939	102	<5	1.246	1.244	512
60	1.934	1.938	401	<5	1.234	1.232	213
		1.937	410			1.231	620
35*	1.812	1.813	202	15*	1.209	1.209	303
		1.813	321			1.208	701
10*	1.740	1.741	411			1.177	223
40*	1.709	1.710	212	10	1.178	1.176	432
20*	1.676	1.678	420			1.176	621
						1.176	710

Note: 114.6-mm Gandolfi camera, CuK α radiation, visually estimated intensities, indexed with the aid of the precession-film data.

* Reflections that were used in the least-squares refinement of the cell parameters.

Chemical data

Laurelite was analyzed with an electron microprobe utilizing synthetic PbF₂ for Pb and F and synthetic PbCl₂ for Cl. Water was determined on a Mitsubishi moisture titrator using a 3.35-mg sample. The water determination indicated that the water is tightly bound, probably in the form of OH. These analyses yielded Pb 82.0, F 13.0, Cl 3.6, OH 0.9 (H₂O 0.5), total 99.5 wt%. The empirical formula based upon F + Cl + OH = 2 is Pb_{0.94}[F_{1.63}Cl_{0.24}OH_{0.13}]_{22.00}. The simplified formula is Pb(F,Cl,OH)₂, which (with F:Cl:OH = 1.63:0.24:0.13) requires Pb 83.25, F 12.44, Cl 3.42, OH 0.89, total 100.00 wt%. Laurelite decomposes rapidly in cold 1:1 HCl and dissolves very slowly in cold water.

Crystallography

No single crystals large enough for X-ray diffraction studies could be found. Because of the growth of needles in parallel bundles and the pervasive twinning on [001], most samples examined by the precession method yielded diffuse streaked reflections about the *c* axis. The crystal used in the cell determination was nearly single, having only one smaller twin crystal attached. Laurelite is hexagonal with possible space groups *P*6, *P*6̄, or *P*6/*m*. The cell parameters refined from the powder data are *a* = 10.252(9), *c* = 3.973(1) Å. The cell volume is 361.7(6) Å³ and *Z* = 6.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuK α radiation was employed and the intensities were visually

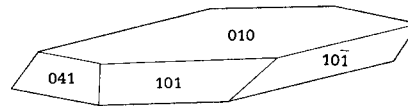


Fig. 3. Crystal drawing of aravaipaite.

estimated. These data, along with the calculated *d* values, are given in Table 3.

Comments on the structure

Laurelite has not yielded crystals adequate for structure determination. However, a structural relationship with α -PbF₂ (as well as the minerals cotunnite, laurionite, paralaurionite, and fiedlerite) is indicated. The intense reflections 210, 140, and 420 on the *hk*0 precession photograph of laurelite are consistent with an orthorhombic pseudocell having *a* = 6.73, *b* = 7.79, and *c* = 3.97 Å. This is analogous to the orthorhombic (pseudo-hexagonal) α -PbF₂ cell, which has *a* = 6.440, *b* = 7.651, and *c* = 3.899. The slightly larger dimensions of the laurelite pseudocell are consistent with the partial replacement of F by Cl. In the α -PbF₂ structure, Pb is 9-coordinated in tri-capped trigonal prisms. These prisms form face-sharing columns parallel to *c*, which are joined by sharing edges.

ARAVAIPAITE (Pb₃AlF₉·H₂O)

Appearance and physical properties

Aravaipaite occurs as thin plates, 0.001 to 0.1 mm thick, and up to 3 mm across. The plates are lamellar on {010}, the only prominently developed face. The {041} face was also detected, but plate edges are usually rounded when not forming contacts with other crystals. A perfect micaceous {010} cleavage was observed, as were good {100}, {001}, {101}, and {10 $\bar{1}$ } cleavages. Figure 3 depicts a single-crystal bounded by the observed faces and cleavages. Polysynthetic twinning on {010} is always present.

Aravaipaite is colorless and has a white streak. It is transparent with a vitreous to pearly luster. No fluorescence in ultraviolet light was detected. The Mohs hardness is about 2. Thin plates are flexible, although not as much so as muscovite. The fracture is irregular.

The density could not be measured, as the mineral sinks rapidly in Clerici solution (ρ = 4.2 g/cm³), and the amount of material available is insufficient for density determination by other means. A cell content of four formula weights (*Z* = 4) was chosen because it provides a reasonable packing efficiency of 62%, compared with 54% for β -PbF₂ and 66% for the compound PbAlF₅. This yields a calculated density of 6.37 g/cm³.

Optical properties

The optical properties of aravaipaite were determined by immersion using a Supper spindle stage. The polysynthetic twinning on {010} is obvious under crossed polarizers and considerably complicated the determination of optical properties. Utilizing the perfect {010} cleavage, a nearly single crystal with a very small attached twin was

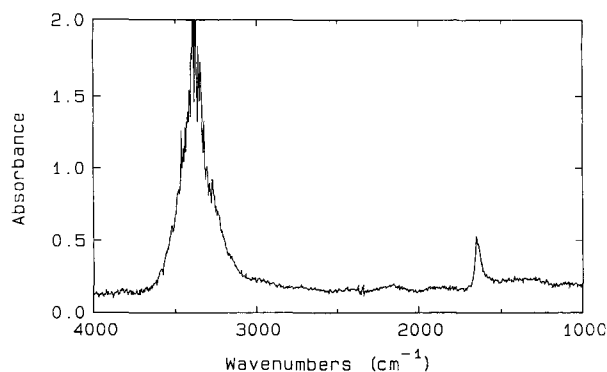


Fig. 4. Single-crystal infrared spectrum of aravaipaite.

obtained for determination of optical properties. Aravaipaite was determined to be biaxial (-). The indices of refraction measured in white light are $\alpha = 1.678(2)$, $\beta = 1.690(2)$, and $\gamma = 1.694(2)$. The observed $2V$ is $70(3)^\circ$; the calculated $2V$ is 66° . Strong dispersion, $r < v$, was observed. The optical orientation is specified by the Euler angles $\phi = 67^\circ$, $\psi = 60^\circ$, $\theta = 76^\circ$. Aravaipaite was stable in the immersion liquids during the period of optical study.

Chemical data

Aravaipaite was analyzed with an electron microprobe utilizing synthetic PbO, hornblende, and synthetic CaF₂ for Pb, Al, and F respectively. The analysis yielded Pb 73.8, Al 3.6, F 21.0, total 98.4 wt%. The amount of aravaipaite available was insufficient for water determination by conventional methods, so recourse was made to single-crystal infrared spectroscopy that required only a single small plate of the mineral. The spectrum (Fig. 4) indicated about 3 wt% water. The uncertainty in this value is judged to be about 1 wt%, principally because of the uncertainty in the molar absorptivity. The intensity of the 1650 cm^{-1} band, corresponding to the H₂O bending mode, is consistent with all water being in the form of molecular H₂O. Anisotropic absorbance in the 3400 cm^{-1} region suggests that the H₂O is structurally bound.

The empirical formula based upon F = 9 is Pb_{2.90}Al_{1.09}F_{9.00} · 1.36H₂O. The simplified formula is Pb₃AlF₉ · H₂O requiring Pb 74.21, Al 3.22, F 20.42, H₂O 2.15, total 100.00 wt%. Aravaipaite decomposes rapidly in cold 1:1 HCl and dissolves very slowly in cold water.

Crystallography

Because of the pervasive {010} polysynthetic twinning, no completely single crystal suitable for X-ray diffraction study could be found. The crystal chosen for the X-ray (and optical) study was nearly single, having only one smaller twin lamella attached. The two intersecting twin lattices were readily apparent on the precession photographs. Aravaipaite is triclinic with possible space groups $P1$ or $P\bar{1}$. The cell parameters refined from the powder data are $a = 5.842(2)$, $b = 25.20(5)$, $c = 5.652(2)\text{ \AA}$, $\alpha =$

TABLE 4. X-ray powder-diffraction data for aravaipaite

<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>hkl</i>
80	12.5	12.5	020	10	2.304	2.301	260
<5	5.78	5.78	110	10	2.263	2.265	162
<5	5.64	5.64	001	10	2.226	2.226	280
10	5.27	5.28	021	25	2.172	2.169	082
25	4.98	4.97	130	10	2.045	2.050	280
5	4.34	4.34	041			2.039	281
		4.01	111			2.030	222
5	4.00	4.00	111			2.029	082
		3.66	131	40	2.028	2.029	202
		3.65	150			2.022	202
70	3.65	3.64	131			1.981	2·10·0
60	3.50	3.50	131	15	1.979	1.978	1·11·1
60	3.33	3.32	151	5	1.946	1.948	310
5	3.240	3.245	141			1.901	1·11·1
100	3.134	3.132	080	10	1.900	1.899	281
5	3.000	2.997	151	10	1.816	1.816	311
		2.920	210			1.816	1·13·1
40	2.916	2.912	200	5	1.790	1.790	341
		2.823	012			1.774	331
40	2.822	2.819	002	5	1.772	1.771	113
		2.590	201			1.760	143
5	2.588	2.584	201	5	1.758	1.757	351
		2.558	221			1.755	331
5	2.561	2.558	221			1.739	143
10	2.505	2.505	0·10·0	20	1.737	1.737	133
		2.415	151			1.737	371
5	2.414	2.414	132	10	1.702	1.702	
		2.354	152	15	1.671	1.673	1·13·1

Note: 114.6-mm Gandolfi camera, CuK α radiation, visually estimated intensities, indexed with the aid of the precession-film data. All reflections were used in the least-squares refinement of the cell parameters.

$93.84(4)$, $\beta = 90.14(4)$, and $\gamma = 85.28(4)^\circ$. The cell volume is $827(2)\text{ \AA}^3$ and $Z = 4$.

The X-ray powder-diffraction pattern was recorded using a Gandolfi camera of 114.6-mm diameter. CuK α radiation was employed and the intensities were visually estimated. These data along with the calculated d values are given in Table 4.

Comments on the structure

Aravaipaite crystals adequate for structure determination were not found. However, a structural relationship with β -PbF₂ is indicated. The formula, cell dimensions, and perfect cleavage suggest that the structure may be based upon layers of the β -PbF₂ (fluorite) structure parallel to {010} with Al(F,H₂O)₆ octahedra between layers. Note that the a and c cell dimensions are 5.842 and 5.652 \AA , respectively, and β is very close to 90° . (The $h0l$ precession photograph is pseudotetragonal.) The unit cell of β -PbF₂ is cubic with $a = 5.940\text{ \AA}$.

GLADSTONE-DALE COMPATIBILITY

The Gladstone-Dale compatibility indices, $1 - (K_p/K_c)$, for grandreefite, pseudograndreefite, laurelite, and aravaipaite are -0.061 , -0.017 , -0.136 , and 0.100 , respectively (Mandarino, 1981). These suggest that the compatibility among the density, average index of refraction, and composition is adequate only for pseudograndreefite.

The Gladstone-Dale relationship should probably not be considered a valid measure of compatibility for these minerals because current knowledge concerning the interaction of Pb with halogen elements is incomplete.

PARAGENESIS

The new minerals are interpreted as resulting from the reaction of supergene solutions with galena and fluorite. This is suggested by their compositions, by their spatial proximity to galena and fluorite, and by the presence of anglesite fracture-filling in the quartz surrounding the vug.

The presence of Pb^{2+} in solution is clearly critical to the formation of the new minerals. Because of the strong tendency of this ion to combine with sulfate or carbonate, its mobility in systems dominated by these anions is very limited. Close proximity of galena to a source of fluoride ion is seemingly necessary for the formation of the new minerals.

Of apparent importance as well is the isolation of the vug from acidic sulfate-rich solutions, which permeated most of the adjacent oxidation zone. Otherwise either anglesite would have formed in preference to the lead fluorides or earlier-formed lead fluorides would have been destroyed by the later solutions. In this regard, it is presumed that the quartz, fluorite, and galena layers on the specimen formed a continuous envelope around the vug. This view is supported by observations on other isolated vugs in the bench area (Wayne Thompson, personal communication, 1988).

The secondary calcium fluoride minerals gearsutite and creedite were reported from the mine by both Jones (1980) and Besse (1981). Besse reported gearsutite to be moderately common in the bench area as a very late stage, chalky cavity filling. Besse (personal communication, 1988) also reported the occurrence of prosopite in an isolated vug in the bench area. None of these minerals is found in association with the new lead fluoride minerals described here, although small amounts of gearsutite are present in the matrix surrounding the vug. The conditions present in this isolated vug must have favored the formation of secondary lead fluorides rather than calcium fluorides, since Ca would have been available from the alteration of the fluorite.

The new minerals probably crystallized from the same supergene solution as it evolved under approximately closed system conditions within the vug. Although the crystallization ranges undoubtedly overlapped considerably, growth interrelationships suggest the following crystallization order: grandreefite \rightarrow pseudograndreefite \rightarrow laurelite \rightarrow aravaipaite. The trend among these minerals is toward decreasing amounts of sulfate and increasing amounts of F and water. The increase in water content follows the normal tendency toward increasing water li-

gation with decreasing temperature. The decrease in sulfate and increase in F suggest that the sulfate was selectively incorporated into the earlier phases. The selective incorporation of Cl in laurelite is probably attributable to the preference of Cl for the α - PbF_2 ($PbCl_2$) structural arrangement. The Al in aravaipaite was probably present in the invading supergene solution and was progressively concentrated as the earlier lead fluoride minerals crystallized.

The combination of conditions that resulted in the formation of these four new minerals thus far appears to have been unique, since only one vug containing these minerals has been recognized during nearly a century of mine operation and a quarter century of intense interest in this mine on the part of mineral collectors. The common association of galena and fluorite in this and countless other deposits throughout the world further testifies to the unusual set of conditions that must have existed for these four minerals to form. It should be noted, however, that the new minerals are inconspicuous in comparison to the brightly colored secondary copper minerals, which are of particular interest to collectors at the Grand Reef mine. Specimens with colorless needlelike crystals consistent in appearance with laurelite have been reported by at least two other persons who have collected minerals at the Grand Reef mine, but they discarded the specimens thinking them insignificant.

ACKNOWLEDGMENTS

We acknowledge contributions to this study by a number of individuals. William Besse brought the type specimen to the attention of A.R.K. Wayne Thompson and Richard A. Bideaux of Southwestern Mineral Associates donated the type specimen. Les Presmyk loaned the second specimen and matrix fragments for examination. William Besse, Wayne Thompson, and David Shannon provided information regarding the geology and mineralogy of the Grand Reef mine. George Rossman of the California Institute of Technology conducted the infrared studies. Larry L. Jackson of the U.S. Geological Survey in Denver conducted the Karl Fischer moisture titration. Charles Ross and Charles Strouse of the University of California at Los Angeles assisted A.R.K. in the crystal-structure investigations of grandreefite and pseudograndreefite.

REFERENCES CITED

- Besse, W.W. (1981) The mineralogy of the Grand Reef mine, Aravaipa mining district, Graham County, Arizona. Master's thesis, Department of Geology, California State University at Los Angeles.
- Fahey, J.A. (1976) Crystal structure of lanthanum oxysulfate. *Proceedings of the 12th Rare Earth Research Conference* (Vail, Colorado), 762-771.
- Jones, R.W. (1980) The Grand Reef mine, Graham County, Arizona. *Mineralogical Record*, 11, 219-225.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441-450.

MANUSCRIPT RECEIVED NOVEMBER 17, 1988

MANUSCRIPT ACCEPTED MARCH 16, 1989